

As the exponential is small,

$$\left(\prod_i \frac{\nu_i}{\nu_{i0}}\right)^{1/3N} = 1 - \gamma_\infty \int_{T_0}^T \beta dT. \quad (17)$$

Thus the integrated form yields the geometric mean of the frequency ratios  $\nu_i/\nu_{i0}$ .

Table 2. Grüneisen constant  $\gamma$  of LiF

Temperature (°C)	$\gamma$
0	1.63
50	1.59
100	1.50
200	1.42
300	1.34
400	1.26
500	1.14
600	0.98
650	0.91
700	0.83
750	0.77
800	0.73
850	0.71

Fig. 4 gives a plot of  $1 - \gamma_\infty \int_{T_0}^T \beta dT$  versus  $T$  for LiF ( $\theta = 617^\circ\text{K}$ ). It is seen that the mean frequency de-

creases by about 13% between 300 and 1000°K. The values of  $\gamma$  at different temperatures are given in Table 2. It is interesting to note that  $\gamma$  decreases with temperature. In calculating  $\gamma$  the values of  $C_p$  used were those given by Douglas & Dever (1954) while the compressibility values were taken from Suss (1958). The accuracy claimed in the case of  $C_p$  and compressibility is about  $\frac{1}{2}\%$ .

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## A Simple Method for Locating Unoccupied Spaces in a Proposed Crystal Structure

BY D. J. WATKIN

*Chemical Crystallography Laboratory, South Parks Road, Oxford OX1 3QS, England*

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The presence of unoccupied space of sufficient cross section lying outside the van der Waals surfaces of the atoms in a crystal structure may mean that atoms have been omitted from the structure. A simple graphical method has been devised to display these voids. When such voids occur because of the omission of atoms from a trial structure, the significance of peaks in the difference map in the region of the void is enhanced. This makes it possible to detect and, within limits, to place poorly resolved atoms.

A common complication in the determination of molecular structures is the unexpected presence of molecules of solvent in the crystal. When the crystal is stable and the molecular formula of the major component is known, the presence of solvent of crystallization can be detected by density and unit-cell measurements. If the density cannot be measured or when the molecular weight of the material is high, difference Fourier maps are relied on to reveal solvent molecules. Comparison of the difference map with the structure is time-consuming for medium-sized structures, especially if the map has an irregular background. Electron density peaks due to atoms with only partial occupancy, large thermal parameters or actual positional disorder

will be low and may not stand out from the background, and then may not be included in the final description of the structure. If solvent is expected, for example by analogy with a related compound, an extended space-filling model of the structure will reveal the possible sites (Powell, Watkin & Wilford, 1971) but this procedure is slow.

A graphic display has been devised to detect the omission of atoms from a structure. Scale drawings of sections through the whole unit cell are generated, with those areas falling within the van der Waals radius of each atom centre shaded in. Any voids within the cell are thus revealed, and the difference Fourier map for this region can be closely examined. A normal

distance and angle calculation will reveal the compatibility of peaks taken from the difference map.

To simplify the calculation of the intersection of lines and planes with the van der Waals spheres, the coordinate system defined by the lower triangular orthogonalization matrix (Rollett, 1965) was used.

$$\mathbf{x} = \mathbf{L}\mathbf{x}$$

$$\mathbf{L} = \begin{bmatrix} a \sin \beta \sin \gamma^* & 0 & 0 \\ -a \sin \beta \cos \gamma^* & b \sin \alpha & 0 \\ a \cos \beta & b \cos \alpha & c \end{bmatrix}$$

The orthogonal cell having the same volume as the crystallographic unit cell has edge lengths given by the diagonal elements of this matrix. All the space-group symmetry operators are applied to the parameter list defining the asymmetric unit and the generated coordinates orthogonalized. Whole-cell translations are applied in order to determine those positions that lie inside the orthogonal cell and within the appropriate van der Waals radius of the surface of this cell. For unit translations parallel to the  $j$ th axis,

$$\Delta \mathbf{x}_i = l_{ij},$$

so that translations parallel to  $\mathbf{b}$  do not affect orthogonal  $\mathbf{x}$ , and translations parallel to  $\mathbf{c}$  do not affect  $\mathbf{x}$  and  $\mathbf{y}$ . Typically a compound having 100 atoms in the unit cell has over 200 atoms that have part of their van der Waals spheres penetrating the cell.

The display consists of sections cut parallel to one face of the orthogonal cell. The equations of the circles of intersection of the section with the van der Waals spheres are calculated, and although these could be fed to a graph plotter or visual display unit, it has proved very convenient to output the sections on a line printer. An equation is set up to represent each line in the printed page, and the points of intersection with the van der Waals circles are determined. A character representing the atom concerned is stored for each printer column within this interval, and when all atoms touching this line have been examined the line is output, and the next line computed. The orthogonal atomic coordinates are scanned at the beginning of each section, and a short list compiled so that only those atoms touching the section need be tested for intersection with the printer lines. The rate-determining stage of the computation is the output of the alphanumeric field, which is therefore kept as small as possible.

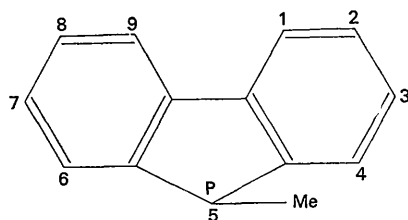


Fig. 1. 5-Methyl-5H-dibenzophosphole.

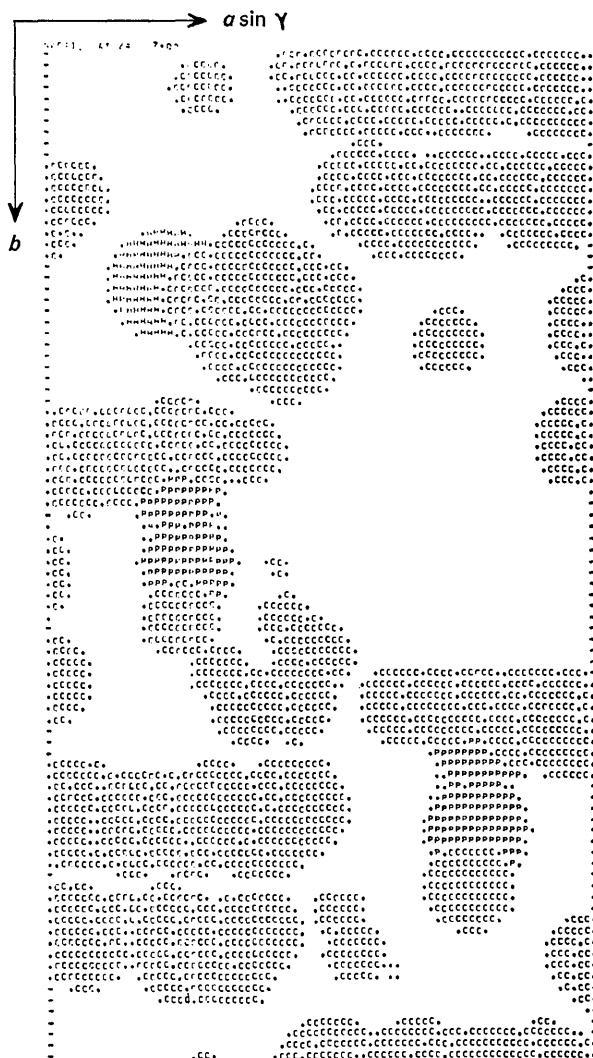


Fig. 2. Section through the orthogonal cell at  $Z = 7.0 \text{ \AA}$ , showing a large void to the right of centre. The first chlorobenzene molecule lies to the left and above the void. C ≡ carbon, H ≡ chlorine, M ≡ nickel, P ≡ phosphorus.

A scale of 1 cm representing 1 Å has been found to give useful and pleasing drawings. At smaller scales the circles cannot be properly generated by the printer grid, though it is still possible to use the drawings for their main purpose. Sections are computed at about 0.7 Å separation.

This program was employed in the solution of the crystal structure of dibromotris(5-methyl-5H-dibenzophosphole)nickel(II) (Fig. 1). The data extends only to a Bragg angle of  $17^\circ$  with Mo  $K\alpha$  radiation ( $40^\circ$ , Cu  $K\alpha$ ), since the collection of further data would have required a quite unjustified expenditure of diffractometer time. The crystals exist in only minute amounts and decompose rapidly in an unenclosed space, and hence had to be preserved by a coating of polyurethane varnish. The asymmetric unit contains two molecules of the complex, the heavier atoms of which are related

by an approximate  $a$  glide plane. Four of the six organic ligands were clearly resolved, being quickly



Fig. 3. The equivalent section to Fig. 2, but with the second solvent molecule included.  $Y \equiv$  chlorine,  $Z \equiv$  carbon.

found by a Fourier map search routine. The remaining two ligands were poorly resolved and least-squares refinement lead to unacceptable bond lengths. A difference Fourier at this stage indicated a molecule of chlorobenzene of solvation, and a large number of peaks in the region of the two ill-defined ligands. The mean plane was calculated through each ligand and an idealized ligand adjusted so as to give as good a fit as possible with the observed atomic positions. Refinement was continued with the bond lengths constrained (Waser, 1963) to reasonable values. At this stage the coordinates were used in the plotting program. A void (Fig. 2) was found with almost the same volume and shape as that containing the previously observed chlorobenzene. Re-examination of the difference Fourier for this region revealed a number of peaks lying approximately in a plane. A mean plane was calculated through these and an idealized chlorobenzene fitted to the peaks. The theoretical coordinates were input to the plotting program together with those for the rest of the structure, and the resulting display (Fig. 3) showed that this solvent molecule neatly fitted the void. The refinement is to be continued. In this example the difference map was particularly uneven, for in addition to the peaks due to anisotropic thermal motion of the 13 heavy atoms there were peaks some of which can be attributed either to large amplitude vibrations of the poorly resolved ligands, or to positional ambiguity for these ligands. There is, however, now no further possibility of finding any more atoms in this structure. The program has also been used in a number of cases to prove the *absence* of solvent molecules from crystal structures.

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